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N. L. Butler
H. G. Hammon
E. S. Jessop
J. R. Kolb
M. O. Riley

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SYNTHESIS AND CHARACTERIZATION OF NEW SILICONE
CONDENSATION POLYMERS

N. L. Butler, H. G. Hammon, E. S. Jessop, J. R. Kolb
and M. O. Riley

Lawrence Livermore National Laboratory*
Livermore, California 94550

ABSTRACT

The LLNL has an active interest in the synthesis of new polysiloxanes as base polymers for cellular silicone materials in very specific design requirements. While the polymers which have been prepared via random equilibration of various cyclic tetrasiloxanes have adequate properties for certain applications, there is evidence to suggest that alternating block polysiloxanes prepared via condensation polymerization techniques have properties more desirable to our end uses as flexible foam materials. The synthetic sequence involves reactions of functionally terminated (amino and hydroxy) polysiloxane oligomers to produce alternating block (ABAB...) materials of high molecular weight dialkylamines as condensation by-products. The analysis and characterization of these block copolymers is reported upon. An additional topic of discussion is the functional endcapping of these poly(dimethyl-diphenyl-methyl vinyl) siloxane copolymers with dimethylvinylsilyl groups. This functional termination should provide a means of tying down any dangling polymer ends present through peroxide crosslinking.

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INTRODUCTION

Cellular silicone materials have been utilized at Lawrence Livermore National Laboratory (LLNL) as support materials, space fillers and shims for many years. Due to a disruption in the commercial availability of the foams as well as silica-filled molding compounds and the base gums upon which these foams are based, LLNL has found it necessary to develop a silicone technology suited to our own needs. We have developed both the synthetic capability for preparation of the base silicone elastomers and the corresponding compounding expertise to convert gums to cellular materials.

The end properties of the flexible foams for which we have the greatest need are low compression set, high load-retention and long service life. There is evidence to suggest that foams based on silicone elastomers which are alternating block copolymers have superior properties to foams based on the standard random equilibration siloxane polymers. While we have developed a synthesis capability based on randomly polymerized siloxanes,¹ we have also generated synthetic techniques for making block copolymer silicone elastomers. This technique is based on sequential condensation reactions between functionally-terminated oligomers. The method of reacting siloxane oligomers which are functionally terminated (silanol/silanol,² silanol/halogen-terminated,² and silanol/amine-terminated,³ for example) is not new. The technique developed here is based on the bulk reaction of amine-terminated and silanol-terminated siloxanes to yield regular, alternating-block copolymers for base elastomers in foam applications.

EXPERIMENTAL

Materials

The cyclotetrasiloxanes (octamethyl, octaphenyl, and sym-tetramethyl-tetravinyl) were purchased from Silar Laboratories, Inc.; Y7005, a silanol-terminated polydimethylsiloxane fluid of approximately 2000 \bar{M}_w was purchased from Union Carbide Corporation; N,N'-bis-(trimethylsilyl)ethylene-

diamine was prepared according to the method of West, Ishikawa and Murai,⁴ 1,7-dichlorooctamethyltetrasiloxane was purchased from Petrarch Chemicals. The initiator tetramethylammonium silanolate $((\text{CH}_3)_4\text{N}^+[\text{O}(\text{Si}(\text{CH}_3)_2\text{O})_4\text{H}]^-)$ or N-catalyst was prepared by reaction of hydrated tetramethylammonium hydroxide with an appropriate amount of octamethylcyclotetrasiloxane at an elevated temperature of $\sim 80^\circ\text{C}$; 1,7-bis(dimethylamino)octamethyltetrasiloxane was prepared from 1,7-dichlorooctamethyltetrasiloxane, dimethylamine and magnesium turnings according to the method of Creamer.⁵

In a typical preparation of amine-terminated prepolymer 998 g (3.36 mole) of octamethylcyclotetrasiloxane, 332 g (0.419 mole) of octaphenylcyclotetrasiloxane, 15 g (.044 mole) of sym-tetramethyltetravinylcyclotetrasiloxane, and 491 g (1.33 mole) of 1,7-bis(dimethylamino)octamethyltetrasiloxane are charged into a reaction vessel and heated with stirring to 100°C . A total of 9.4 g (0.50 wt%) N-catalyst is added via syringe to the heated reaction mixture in two portions, one hour apart. The ring opening polymerization to produce a dimethylamino-terminated prepolymer of $\sim 2000 \bar{M}_w$ is continued for four hours after which the pot temperature is raised to 150°C to deactivate the N-catalyst. The reaction mixture was cooled, and then filtered under a dry inert atmosphere to remove particulates.

Stoichiometric quantities based on screening reactions of Y7005 (silanol-terminated polydimethylsiloxane) and the dimethylamino-terminated prepolymer were mixed in a Baker-Perkins sigma-bladed mixer at approximately 200°F . The reactants were allowed to polymerize to a gum of approximately 500,000 molecular weight before an excess of the endblocking reagent, N,N'-bis(trimethylsilyl)ethylenediamine was added. After an additional 30 minutes of mixing the product was washed three times with distilled water and then dried in vacuo ($80^\circ\text{C}/0.5 \text{ mm}$) for 15 hours to remove any residual water or dimethylamine. Alternatively, vinyl endcapping could be achieved by reaction between the terminal silanol functionality and either vinyltrimethylchlorosilane or vinyltrimethyl (N-methylacetamido)silane. The reaction times with this endcapper and subsequent operations were identical to those employed immediately above.

Polymers were characterized by GPC, and spectroscopic techniques to determine methyl, phenyl, and vinyl contents.

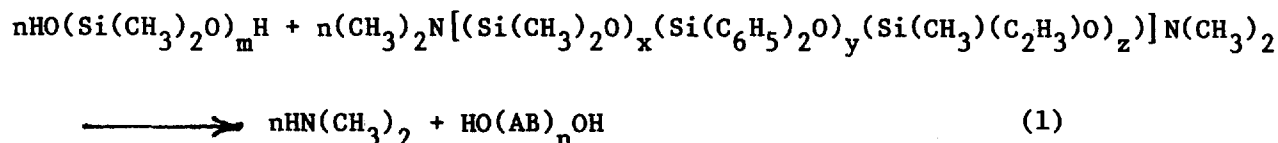
RESULTS AND DISCUSSION

The ultimate use for polysiloxane resins at LLNL is as base materials for silicone flexible foams. The starting polysiloxane resins are reinforced with silica fillers of high surface area and activity, aged and temporarily filled with a soluble filler such as urea. The temporarily filled material is then catalyzed with 2,5-dimethyl-2,5-bis(tertiarybutylperoxy)hexane and mold-cured to the desired shape. The filler is then washed from the crosslinked matrix with hot water leaving behind a cushion of density determined by the amount of temporary filler incorporated initially. While we have formulated flexible foams from polysiloxanes synthesized in a random equilibration manner,¹ compression set data (the lack of recovery to free thickness a foam incurs as a result of a load applied for a finite period of time) indicate these condensation, block polysiloxanes have superior properties. We believe the increased regularity of these alternating block copolymers is most likely responsible for the increased load retention and decreased compression set of the cushions.

The major advantage of the preparative method indicated here is the smooth one-step preparation of the amine-terminated block, block A. This is accomplished by the reaction of the octamethyl-, octaphenyl-, and tetramethyl-tetravinylsiloxanes, N-catalyst and 1,7-bis(dimethylamino)-tetrasiloxane at elevated temperatures. \bar{M}_w is controlled here by the relative amount of chain terminator added. The catalyst is simply deactivated by increasing reaction temperature until the N-catalyst decomposes. This yields block A which is in reality a low \bar{M}_w oligomer of the random equilibration polysiloxanes. All of the diphenylsiloxane units (included to avoid crystallization problems) and methylvinylsiloxane units (included for crosslinking through vinyl moieties) are built into this block.

Block B is a commercially available silanol-terminated polydimethylsiloxane of $\sim 2000 \bar{M}_w$. Both blocks A and B are of approximately equivalent \bar{M}_w so that the alternating blocks are of roughly equal size.

The actual polymerization reaction is given in equation 1.



The polymer composition was examined for the presence of each type of organic group via continuous wave nmr spectroscopy. Gel permeation chromatography was used to characterize polysiloxane \bar{M}_w , \bar{M}_n and polydispersity. The targets for this material were an \bar{M}_w of 500,000, a phenyl content of 12.5% (as $\text{Si}(\text{C}_6\text{H}_5)_2\text{O}$), a vinyl content of 0.4% (as $\text{Si}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{O}$) and trimethylsilyl endcapping. We have achieved a \bar{M}_w of 454200, \bar{M}_n of 208300 (MWD=2.18) with a vinyl content of 0.4%, a phenyl content of 12.6% and a dimethylsiloxane content of 87.0%.

Because of the possibility that long, dangling chain ends may become entangled due to temporary proximity enforced upon them by compression, we decided to incorporate functionality in the endcapping by inclusion of vinyl groups. This was attempted by reaction of the silanol-terminated polymers with vinyltrimethyl-N-methylacetamide and the dimethylvinylsilyl-terminated block copolymers. The vinyl groups were incorporated so that the chain ends could be tied down by crosslinking through reaction with the vinyl-specific catalyst mentioned above. Because of the minute concentration of vinyl introduced in this manner, it has been difficult to obtain direct proof of vinyl endblocking so far. Normal endcapping was accomplished by reaction of the silanol-terminated polysiloxanes with N,N'-bis(trimethylsilyl)ethylene-diamine to yield ethylene diamine and trimethylsilyl-terminated polysiloxanes. Thorough washing of all these systems with water is mandatory to remove byproduct amines which may be responsible for reversion of certain polysiloxanes.

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